

Influence of Smectite Hydration and Swelling on Atrazine Sorption Behavior

MARK A. CHAPPELL,^{*,†} DAVID A. LAIRD,[‡] MICHAEL L. THOMPSON,[†] HUI LI,[§] BRIAN J. TEPPEN,[§] VANEET AGGARWAL,[§] CLIFF T. JOHNSTON,[¶] AND STEPHEN A. BOYD[§]

Department of Agronomy, Agronomy Hall, Iowa State University, Ames, Iowa, 50011, National Soil Tilth Laboratory, USDA-ARS, Ames, Iowa, 50011, Department of Agronomy, Agronomy Hall, Iowa State University, Ames, Iowa, 50011, Department of Crop and Soil Sciences, Michigan State University, East Lansing, Michigan 48824-1325, Department of Crop and Soil Sciences, Michigan State University, East Lansing, Michigan 48824-1325, Department of Crop and Soil Sciences, Michigan State University, East Lansing, Michigan 48824-1325, Crop, Soil and Environmental Sciences, Purdue University, West Lafayette, Indiana 47907-2054, and Department of Crop and Soil Sciences, Michigan State University, East Lansing, Michigan 48824-1325.

Smectites, clay minerals commonly found in soils and sediments, vary widely in their ability to adsorb organic chemicals. Recent research has demonstrated the importance of surface charge density and properties of exchangeable cations in controlling the affinity of smectites for organic molecules. In this study, we induced hysteresis in the crystalline swelling of smectites to test the hypothesis that the extent of crystalline swelling (or interlayer hydration status) has a large influence on the ability of smectites to adsorb atrazine from aqueous systems. Air-dried K-saturated Panther Creek (PC) smectite swelled less ($d(001) = 1.38$ nm) than never-dried K-PC ($d(001) = 1.7$ nm) when rehydrated in 20 mM KCl. Correspondingly, the air-dried-rehydrated K-PC had an order of magnitude greater affinity for atrazine relative to the never-dried K-PC. Both air-dried-rehydrated and never-dried Ca-PC expanded to approximately 2.0 nm in 10 mM CaCl_2 and both samples had similar affinities for atrazine that were slightly lower than that of never-dried K-PC. The importance of interlayer hydration status in controlling sorption affinity was confirmed by molecular modeling, which revealed much greater interaction between interlayer water molecules and atrazine in a three-layer hydrate relative to a one-layer hydrate. The entropy change on moving atrazine from a fully hydrated state in the bulk solution to a partially hydrated state in the smectite interlayers is believed to be a major factor influencing sorption affinity. In an application test, choice of background solution (20 mM KCl versus 10 mM CaCl_2) and air-drying treatments significantly affected

atrazine sorption affinities for three-smectitic soils; however, the trends were not consistent with those observed for the reference smectite. Further, extending the initial rehydration time from 24 to 240 h (prior to adding atrazine) significantly decreased the soil's sorption affinity for atrazine. We conclude that interlayer hydration status has a large influence on the affinity of smectites for atrazine and that air-drying treatments have the potential to modify the sorption affinity of smectitic soils for organic molecules such as atrazine.

Introduction

Atrazine (2-chloro-4-(ethylamino)-6-isopropylamino-1,3,5-triazine) is one of the most widely used selective herbicides in commercial agricultural operations throughout the world. Because of its widespread use, atrazine is frequently found as a pollutant in lakes, rivers, and groundwater, often in concentrations exceeding the $3 \mu\text{g L}^{-1}$ federal drinking water standard (1, 2). The recently recognized ability of atrazine to behave as an endocrine disrupter in mammals (3) and aquatic life (4, 5) emphasizes the need to understand the fate of atrazine in the environment.

Atrazine is a weak base ($\text{p}K_a = 1.68$) and has a relatively low solubility (33 mg L^{-1}) in water. Because of its relatively hydrophobic nature, atrazine was assumed for many years to be primarily adsorbed by soils through partitioning of the atrazine into soil organic matter (6–8). In the early 1990s, however, new understanding about the nature of clay mineral surfaces raised awareness of the fact that soil clays can also play a prominent role in determining the fate of atrazine and other weakly polar organic molecules in soil environments. Lee et al. (9) demonstrated an inverse relationship between sorption of aromatic compounds from aqueous systems and the layer charge of organic-modified smectites (saturated with tetramethylammonium ions). The authors suggested that the aromatic molecules were interacting directly with the siloxane surfaces between charge sites. These results prompted Jaynes and Boyd (10) to use various aromatic compounds to further probe the nature of the siloxane surfaces of organic-modified smectites and to conclude that the siloxane surfaces of the smectites must have some hydrophobic character. Shortly thereafter, Laird et al. (11) demonstrated that Ca-smectites could adsorb from zero to 100% of added atrazine from mildly acidic ($\text{pH} = 4.8\text{--}6.5$) aqueous solutions. In this study, an inverse relationship was observed between the sorption affinity for atrazine and layer charge of the smectites. Because the pH of the systems was well above the $\text{p}K_a$ of atrazine, the authors argued that atrazine was sorbed as a neutral species through hydrophobic interactions with molecular scale uncharged regions on the siloxane surfaces. Later, Laird and Fleming (12) probed the nature of smectite surfaces with 3-butylpyridine and found clear evidence for sorption of the ionic species at pHs below the $\text{p}K_a$ and sorption of molecular species for pHs above the $\text{p}K_a$ of the 3-butylpyridine. Adsorption of the molecular species was attributed to a combination of hydrophobic interactions involving uncharged nanosites on the siloxane surfaces and polar interactions involving the ring N and water molecules solvating the interlayer cations. Other workers have found that smectites have substantial potential for sorption of a wide range of weakly polar and nonpolar organic compounds (13).

The type of exchangeable cations on the clay surfaces influences the affinity of smectites for atrazine. For example,

* Corresponding author phone: (515)294-3694; fax: (515)294-3163; e-mail: machap@iastate.edu.

[†] Iowa State University.

[‡] USDA-ARS.

[§] Michigan State University.

[¶] Purdue University.

less atrazine was retained by a Ca-smectite than a mixed ion (9:1 Na:Ca) smectite (14). Potassium-saturated smectite exhibited a higher sorption affinity (K_F) for atrazine than Ca-smectite (15). Fe-saturated Wyoming bentonite had nearly 100 \times greater affinity for atrazine than its Ca-saturated counterpart (16). Similarly, smectite saturated with Al^{3+} had a much higher affinity for atrazine than Ca-smectite (17). Conversely, introduction of charged $Al_y(OH)_x$ polymers decreased the affinity of atrazine sorption by montmorillonite (18).

Smectites exist in multiple hydration phases, variously having 0, 1, 2, 3, or 4 discrete layers of interlayer water molecules. Crystalline swelling describes the process whereby a smectite transitions between two or more of these hydration phases. The extent of crystalline swelling for a smectite is influenced by properties of the smectite (e.g., total layer charge and percentages of tetrahedral charge), nature of the interlayer cations (e.g., valence and hydration energy), and the activity of water in the equilibrating solution or atmosphere. Activation energy barriers stabilize each hydration phase, causing hysteresis in crystalline swelling (19, 20). Hysteresis in crystalline swelling is believed to be the primary cause of hysteresis in cation exchange reactions (21, 22). In this study, we hypothesize that the extent of crystalline swelling of a smectite and hysteresis in crystalline swelling influence the affinity of a smectite for atrazine.

Smectite is the dominant clay mineral in many soils. Thus, it is reasonable to hypothesize that conditions or treatments that influence properties of smectites in soils will also influence the affinity of soils for atrazine. Soils regularly cycle through seasonal periods of wetting and drying, which may affect the hydration status of soil smectites. Furthermore, most soil samples are routinely air-dried and later rehydrated before use in laboratory sorption experiments, and several different salt solutions have been used as background electrolytes in sorption studies. Such treatments have the potential to influence the properties of soil smectites. Several studies have evaluated the effect of rehydration and length of rehydration time on atrazine sorption. Rewetting of an air-dried soil typically occurs as a bimodal process: rapid rehydration followed by a prolonged rehydration stage (23), indicative of intraparticle diffusion by water. These stages of rewetting are often reflected in the rates of pesticide uptake (24, 25). Both atrazine sorption affinity (K_F) and sorption-desorption hysteresis were shown to increase with the length of soil rehydration times (26, 27).

The overall goal of our research is to elucidate mechanisms of interaction between organic molecules and surfaces of soil minerals. The specific objectives of this study were (1) to determine whether changes in crystalline swelling of a reference smectite, induced by sample handling (e.g., air-drying), influences sorption of atrazine by the smectite and (2) to assess whether sample handling (e.g., air-drying and choice of KCl or $CaCl_2$ for a background electrolyte solution) affects atrazine sorption by smectitic soils.

Materials and Methods

Reagents. Atrazine (99% purity) was obtained from Chem Service (West Chester, PA) and used as received. A.C.S.-certified dimethyl sulfoxide (DMSO), methanol (MeOH), acetonitrile, and potassium phosphate were obtained from Fisher Scientific (Madison, WI). Methanol and acetonitrile were HPLC quality.

Sample Preparation. Panther Creek (PC) bentonite was obtained from the A. D. Scott mineral collection at Iowa State University. The PC is a low-charge beidellite (surface charge density = $1.42 \mu mol_C m^{-2}$, 52% tetrahedral charge, (11)). For the study, the raw PC ore was first washed with 0.5 M NaCl, and then the clay-size fraction ($<2.0 \mu m$ esd) was collected by sedimentation. Suspensions of $<2.0 \mu m$ Na-PC were

transferred to Spectra/Por membrane tubing (MWCO 4–6000) and initially dialyzed against 100 mM $CaCl_2$ or 200 mM KCl. When the Na concentrations in the equilibrating solution decreased to approximately $1 mg L^{-1}$, the samples were equilibrated with dilute $CaCl_2$ (5 mM) or KCl (10 mM) to prepare the final Ca-PC and K-PC suspensions. Portions of the Ca-PC and K-PC suspensions were stored at 4 °C (referenced as the “never-dried sample” or “ND treatment”). Another portion of each suspension was transferred to a rectangular plastic tub. Filtered ($0.45 \mu m$) air was pumped through a hose and blown onto the suspension to facilitate air-drying. The clays were air-dried until a solid “cake” was formed. The air-drying process took approximately 1 week depending on the volume of suspension. After drying, the clay was collected and crushed in an agate mortar, and then the air-dried clays were resuspended in and dialyzed against the dilute $CaCl_2$ or KCl solutions (referenced as the “air-dried, resuspended sample” or the “AD treatment”). The treated clays were stored as suspensions for approximately 2 months at 4 °C before their use in the atrazine sorption experiments.

Surface-horizon samples of three smectitic soils, Sparta (sandy, mixed, mesic, Entic Hapludoll), Sperry (fine, montmorillonitic, mesic Typic Argialboll), and Zook (fine, montmorillonitic, mesic, Cumulic Haplaquoll), were collected from Story and Marshall counties in Iowa. After field collection, one portion of each sample was sealed in airtight plastic bags and stored at 4 °C (referenced as never-dried or the ND treatment). ND soil aggregates were broken up by hand as needed but were otherwise used without further processing. Another portion of each soil sample was air-dried, crushed in an agate mortar, and passed through a 2-mm sieve prior to use (referenced as air-dried or AD treatment).

XRD Analysis. A special liquid sample cell was constructed to measure the basal spacings of clay minerals in suspensions. The cell was similar to that described by ref 28 except that the cell was designed for operation in reflection mode rather than transmission mode. The clay suspensions (20 mg clay mL^{-1} water) were analyzed with a Siemens D5000 X-ray diffractometer using $CuK\alpha$ radiation, with a step size of 0.05 degrees and a dwell time of 108–120 s per step (the analysis took approximately 4 h per sample). The cell was tested by analyzing a suspension of a reference glauconite that gave the anticipated 1.0-nm peak. All of the studied clays remained dispersed throughout the analysis period except the air-dried, resuspended Ca-PC, which settled to the bottom of the sample cell after about 1 h. For this sample, the analysis was halted every 30 min to redisperse the sample by shaking.

Atrazine Sorption Experiments. A volume of the cation-saturated PC clay suspensions were added to 30-mL Nalgene Teflon tubes containing dilute $CaCl_2$ (10 mM) or KCl (20 mM) background electrolyte to give a final solid-solution ratio of $12.5 mg mL^{-1}$ (or 250 mg of solids in 20 mL of solution). Aliquots of a concentrated atrazine solution, containing 30 $mg L^{-1}$ atrazine in 96% water + 4% methanol cosolvent (v/v), were then added to the tubes to give initial concentrations of 0, 2.1, 4.2, 5.1, 7.2, and 10.5 $mg atrazine L^{-1}$, which contained 0.3, 0.6, 0.7, 1.1, and 1.4% methanol. Afterward, the atrazine-containing suspensions were equilibrated on a rotary shaker (70 rpm) for 24 h and then centrifuged at 6722g for 10 min. The clear supernatant was analyzed for atrazine. The amount of atrazine sorbed was calculated by subtraction. For quality-control purposes, sorbed atrazine was extracted from the clay samples and analyzed separately. The extractant was a 60:40 mixture of dimethyl sulfoxide (DMSO) and 10 mM $CaCl_2$ (adjusted to pH 9.5 using saturated $Ca(OH)_2$). The clay samples were resuspended in the extractant by vortexing for 30 s and then equilibrating for 1 h on a rotary shaker. After centrifugation (6722g for 10 min), the supernatant was decanted and analyzed for atrazine and atrazine degradation

TABLE 1. Selected Physical and Chemical Characteristics of Three Iowa Soils

	Sparta	Sperry	Zook
clay-silt-sand (%)	15-32-53	25-73-2	43-42-15
organic C (mg kg ⁻¹)	1600	2100	2100
pH ^a	6.2	7.1	5.9
Σ ex. ^b cations	15.5	15.7	29.8
ex. Al (cmol kg ⁻¹)	0.2	0.1	0.1
ex. Ba (cmol kg ⁻¹)	0.0	0.1	0.1
ex. Ca (cmol kg ⁻¹)	12.2	11.1	24.7
ex. K (cmol kg ⁻¹)	0.5	0.9	0.4
ex. Mg (cmol kg ⁻¹)	2.6	3.4	4.1
ex. Na (cmol kg ⁻¹)	0.1	0.2	0.3

^a 1:1 water/soil. ^b Ex. = exchangeable. Obtained by adding 30 mL of 0.2 M NH₄Cl to a 50-mL polypropylene centrifuge tube containing 4 g of air-dried soil. The tubes were shaken for 1 h on a side-to-side shaker and then were centrifuged for 10 min at 9000 rpm. Clear supernatant was collected, and then the soil was rewashed with NH₄Cl solution for a total of three times. Supernatant from the three consecutive washes was analyzed by ICP.

products hydroxyatrazine (HA), desethylatrazine (DEA), and deisopropylatrazine (DIA) by HPLC. The extraction procedure was repeated three or four times for each sample. Total recovery of the sorbed atrazine averaged 98% (ranging from 78 to 114% recovery). No HA, DEA, or DIA was detected in either the supernatant for the adsorption experiment or extracted solutions.

Both air-dried and never-dried soil samples (4 g) were suspended in dilute CaCl₂ (10 mM) or KCl (20 mM) and equilibrated on a rotary shaker for 24 h prior to the addition of atrazine. Otherwise, the procedure used to investigate atrazine sorption by the soils was similar to that described above for the clay samples. Selected chemical and physical properties of the soils used in this study are presented in Table 1. In separate experiments, the effect of soil rehydration time on atrazine sorption was tested by suspending air-dried Sparta soil in dilute (20 mM) CaCl₂ and allowing the suspensions to equilibrate for 24, 109, or 240 h on a side-to-side shaker. Afterward, atrazine was added and the soil suspensions were equilibrated for an additional 24 h. Sorbed atrazine was quantified as described above.

All atrazine sorption experiments for PC and soils were conducted in triplicate.

Atrazine Analysis. Atrazine concentrations were quantified by reverse-phase-high-performance liquid chromatography (RP-HPLC). Chromatographic separations were carried out using a Hewlett-Packard 1050 series HPLC with UV-detection (223 nm) and an Alltech (Alltech Associates, Inc., Deerfield, IL) Platinum EPS C18 column (250-mm length, 4.6-mm i.d., 100 Å pore size, 5-μm particle size). The mobile phase consisted of a mixture of (A) 10 mM KH₂PO₄ (adjusted to pH 3 with concentrated *o*-phosphoric acid) and (B) acetonitrile. The gradient elution was initially 80:20 (A to B) and graded linearly to 60:40 (A to B) over an 8-min run. The elution rate was 1 mL min⁻¹. The method was calibrated with reagent grade atrazine over the range of 0.6–10.5 mg L⁻¹ ($R^2 = 0.9998$).

Data Analysis. A weighted nonlinear regression was used to fit the measured sorption data to the modified Freundlich equation (29):

$$C_s = K_F' C_r^n$$

where C_s is the amount of atrazine sorbed at equilibrium (μmol kg⁻¹), C_r is the reduced concentration of atrazine; a unitless ratio of the equilibrium solution atrazine concentration (μmol L⁻¹) to the molar solubility of atrazine (μmol L⁻¹), K_F' is the modified Freundlich sorption affinity constant (μmol kg⁻¹), and n is the coefficient of linearity (unitless). Tests for

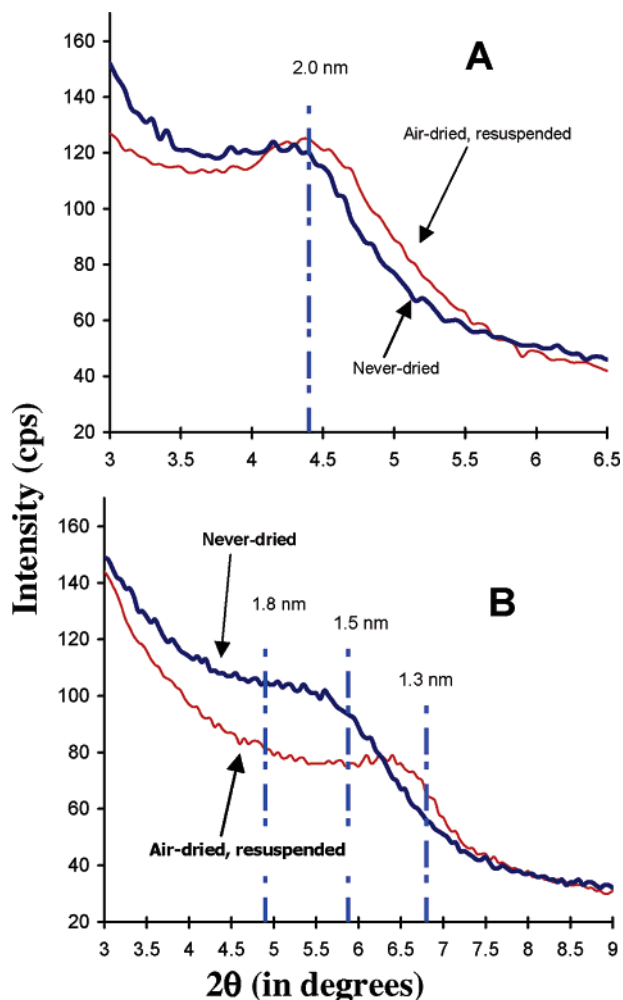


FIGURE 1. X-ray diffractograms of (A) Ca-PC and (B) K-PC clay suspension (θ refers to the angle of incident X-rays on the sample, in degrees).

significant differences among K_F' values were evaluated using a pooled t-test. All statistical analyses and nonlinear fitting were done using SAS (SAS Institute, Cary, NC).

Molecular Simulations. A model for a K-saturated smectite was created and molecular dynamics simulations of atrazine-clay complexes were performed to explore the interactions between atrazine, cations, and water in the interlayer region. The composition of the model smectite was $K_7(Al_{42}Mg_6)(Si_{96}Al_1)O_{240}(OH)_{48}$ with a CEC of 79 cmol kg⁻¹. One molecule of atrazine was added to each unit cell of the smectite, with the atrazine ring perpendicular to the basal planes of the clay. The simulated loading rate was therefore 24 mg atrazine per gram clay for the smectite systems. Water molecules were also added (in random interlayer positions) so that constant-pressure simulations resulted in either 12.4 or 17.3 Å clay layer spacings. The energies were computed using a force field developed for clays (30) combined with the polymer consistent force field or pcff (31, 32) for the organics and water. The molecular dynamics simulations were run in the NPT-ensemble for 0.1 ns, much longer than the time required for the system volume and energy to equilibrate.

Results and Discussion

Panther Creek Smectite. X-ray diffraction analysis of never-dried Ca-PC aqueous suspensions revealed a very broad d_{001} peak centered on 2.1 nm (Figure 1A). The 2.1-nm basal spacing indicates that the never-dried Ca-PC was dominated

by domains with four layers of interlayer water molecules. The very broad nature of the XRD peak was caused both by the random orientation of clay quasicrystals in the suspensions and by disorder in the layer stacking sequence. Previous XRD analysis of Ca-PC prepared as air-dried oriented films showed a basal spacing of 1.5 nm (11), which indicates only two layers of interlayer water molecules. Thus, in an aqueous suspension, Ca-PC interlayers are much more expanded and more fully hydrated than in the air-dry state, typically analyzed by XRD. This distinction is important, because during an adsorption experiment the solute "sees" the more fully hydrated clay and must compete with water molecules for adsorption into the expanded interlayers.

The air-drying treatment undoubtedly causes the AD Ca-PC to collapse to 1.5 nm, but it is evident from Figure 1A that the AD Ca-PC reexpanded to 2.0 nm when resuspended. The XRD peak for the AD Ca-PC suspension is shifted slightly to the right (2.0 versus 2.1 nm) and is slightly less broad than the XRD peak for the ND Ca-PC suspension. These differences indicate that the coherently diffracting domains in the AD Ca-PC suspensions were larger and more ordered than the domains in the ND Ca-PC suspensions. However, it is clear that both the AD and the ND Ca-PC samples are dominated by interlayers with four layers of interlayer water molecules.

X-ray diffraction patterns for the AD and ND K-PC clay suspensions are presented in Figure 1B. The XRD peaks (shoulders) for the K-PC suspensions are even broader and more diffuse than the peaks observed for the Ca-PC suspensions. The XRD peak for the ND K-PC suspension is centered on approximately 1.7 nm, which is close to the anticipated peak position for a smectite dominated by three layers of interlayer water molecules (1.75 nm). By contrast, the XRD peak for the AD K-PC suspension is centered at approximately 1.38 nm, which is about halfway between the anticipated peak positions for a two-layer hydrate (1.50 nm) and a one-layer hydrate (1.25 nm). The results indicate random interstratification of layers with one and two layers of interlayer water molecules in the AD K-PC suspension.

Consistent with previous literature (15), the K-PC had a much greater affinity for atrazine than the Ca-PC (Figure 2; Table 2). In addition, the results of this study demonstrate for the first time that the extent of crystalline swelling of a smectite has a large influence on atrazine sorption affinity. The air-dried K-PC had almost an order of magnitude greater affinity for atrazine relative to the never-dried K-PC. By contrast, atrazine sorption on Ca-PC (Figure 2) was not significantly affected by air-drying (Table 2), and air-drying had little or no effect on the extent of crystalline swelling for the Ca-PC. These results support our hypothesis linking the extent of crystalline swelling with sorption affinity of smectites for atrazine. In addition, these results suggest that the sorption affinity of a smectite for atrazine is more reliably predictable by the hydration status of clay interlayers than by simply considering the nature of the saturating cation.

Atrazine interacts with smectite surfaces through a variety of bonding mechanisms (33). The lone pair electrons of the ring N atoms may form hydrogen bonds with water molecules, especially those solvating the exchangeable interlayer cations. At the same time, the alkyl tails of the atrazine molecule may interact with hydrophobic nanosites on the smectite basal surfaces, that is, valence-satisfied basal oxygens located between charge sites. Molecular modeling revealed likely orientations of atrazine in the interlayers of smectite with one and three layers of interlayer water molecules (Figure 3). For a smectite with only one layer of interlayer water, atrazine is oriented parallel to the basal surfaces and interacts directly (no intervening water molecules) and simultaneously with hydrophobic nanosites on opposing basal surfaces. For a more expanded smectite with

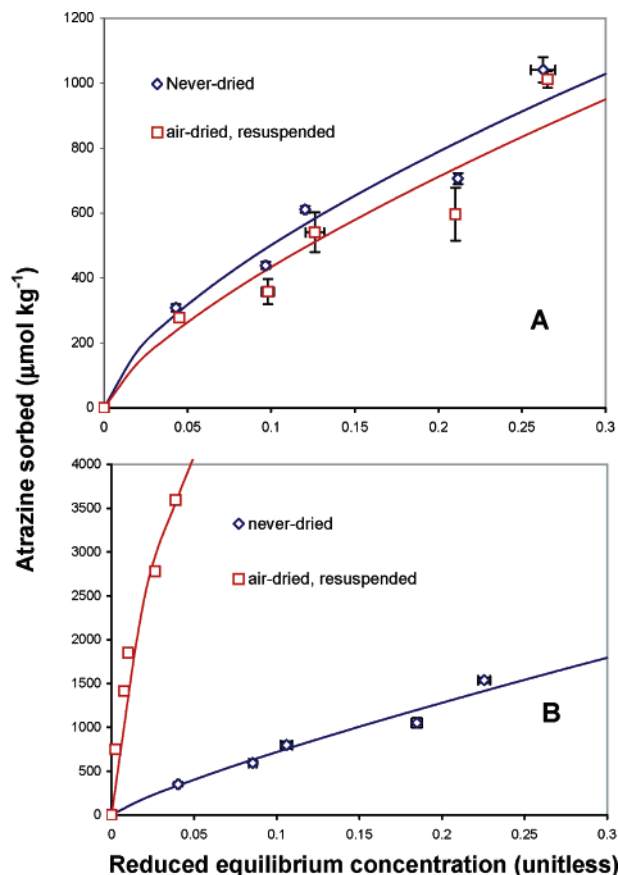


FIGURE 2. Atrazine sorption isotherms for (A) Ca-PC and (B) K-PC clay suspensions. Reduced concentrations are concentrations normalized by the aqueous solubility (29).

TABLE 2. Regression Coefficients Calculated from the Nonlinear Fit of the Modified Freundlich Equation to the Atrazine Sorption Data

material	cation	handling	K_F	K_F st. error	n	r^2
PC	Ca	ND ^a	2263	108	0.66	0.99
		AD ^b	2248	154	0.72	0.98
	K	ND	4893	754	0.83	0.99
		AD	20 956	2217	0.55	0.99
Sparta	Ca	ND	114	5	0.67	0.99
		AD	249	22	0.91	0.98
	K	ND	160	14	0.83	0.99
		AD	283	4	0.87	1.00
Sperry	Ca	ND	462	10	1.25	1.00
		AD	265	26	0.99	0.98
	K	ND	247	10	0.87	1.00
		AD	247	1	0.94	1.00
Zook	Ca	ND	277	39	0.83	1.00
		AD	474	30	0.99	0.99
	K	ND	380	12	0.86	1.00
		AD	374	3	0.85	1.00

^a ND = never-dried. ^b AD = air-dried, resuspended.

three layers of interlayer water molecules, the atrazine is inclined at an acute angle relative to the basal surfaces. The two alkyl side chains interact directly with one basal surface each. This configuration appears to be at least partially stabilized by H-bonds between amino hydrogens and the smectite basal oxygen atoms; two such bonds of 2.5 and 2.6 Å formed between one amino group and one basal surface and were then stable for the remainder of the simulation. The rest of the atrazine molecule is forced to interact with interlayer water molecules. For atrazine sorption on smec-

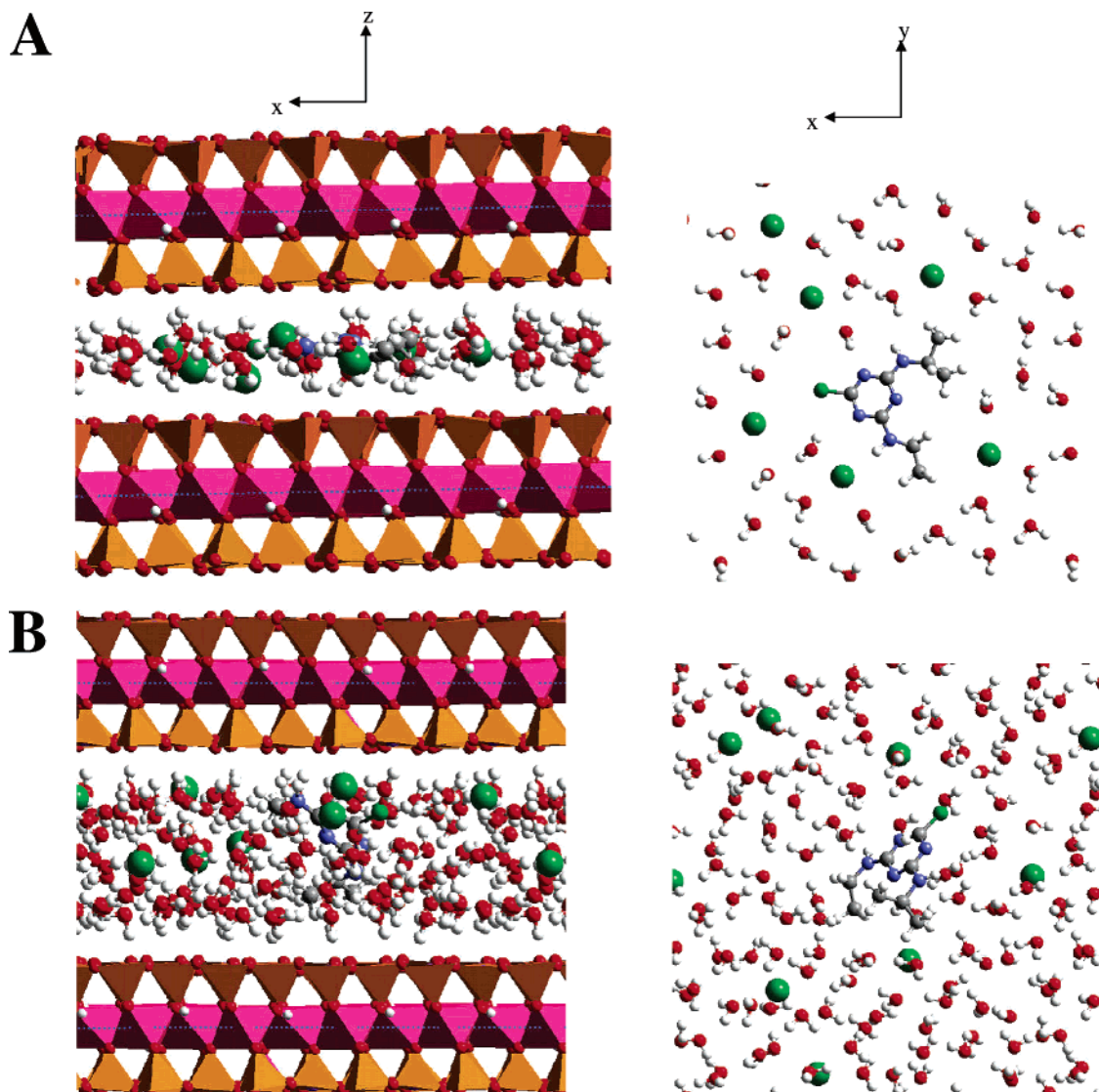


FIGURE 3. Snapshot showing the orientation of atrazine within the interlayer of a K-saturated smectite containing (A) one and (B) three layers of hydration water. (red = oxygen, white = hydrogen, blue = nitrogen, gray = carbon, green = interlayer K⁺ cations). Images on the left depict a side view (*x, z* plane) of the atrazine–smectite interlayer complex while the images on the right depict the same from a top view (*x, y* plane), having removed the upper silicate layer.

tites, the entropy increase on removing atrazine from a fully hydrated state in the bulk solution to a lesser-hydrated state in the smectite interlayer is believed to contribute to the free-energy change for the system. This effect is similar to capillary condensation of hydrophobic solutes (34), in which the free energy of sorption becomes more favorable as pores in the adsorbent become smaller. In this case, the smectite interlayer is a slit-pore and the optimal thickness for adsorption of hydrophobic molecules is approximately the molecular thickness, which corresponds (for aromatic molecules) to *d* spacings near 12.5 Å. Therefore, the difference in hydration status of atrazine in the interlayers is believed to account for the dramatic effect of crystalline swelling on the affinity of smectites for atrazine (Figures 1 and 2). Another way of stating this is that the monolayer is an interlayer phase (22) that is much more conducive to hydrophobic organic solute partitioning from water than are other, more hydrated and expanded, interlayer phases.

Smectitic Soils. XRD analysis (see online Supporting Information) revealed that the clay fraction of the soils was dominated by smectite. Results for the Panther Creek smectite raise concerns that the reliability of atrazine sorption data for smectitic soils may be adversely affected by sample

handling. Therefore, three smectitic soils were analyzed using air-dry and never-dry pretreatments. Although the soil samples were not saturated with Ca or K prior to the adsorption analysis, we did conduct the sorption experiments using both CaCl₂ and KCl background solutions. Clay content, the most important difference among the soil samples, ranged from 15% in the Sparta to 43% in the Zook (Table 1). Organic C levels were similar in the Sperry and Zook and slightly lower in the Sparta. Calcium was the dominant cation on the exchange complex of all three soils (from 71 to 83% of CEC), followed by Mg (14 to 21% of CEC), and K (1.2 to 5.4% of CEC).

An example of the atrazine sorption isotherms obtained in these experiments is shown in Figure 4. The trends in the data were variable. Significantly ($P < 0.025$) higher K_F' values were obtained for sorption of atrazine on the AD Sparta and AD Zook rehydrated in CaCl₂ relative to the ND Sparta and ND Zook (Table 2). In contrast, ND Sperry in CaCl₂ had a significantly higher K_F' than AD Sperry rehydrated in CaCl₂. Also, the *n* value for ND Sperry in CaCl₂ was greater than 1.0. In dilute KCl, the AD Sparta exhibited a significantly higher K_F' value than ND Sparta, but the K_F' values for the AD Sperry and AD Zook soils were not significantly different from the

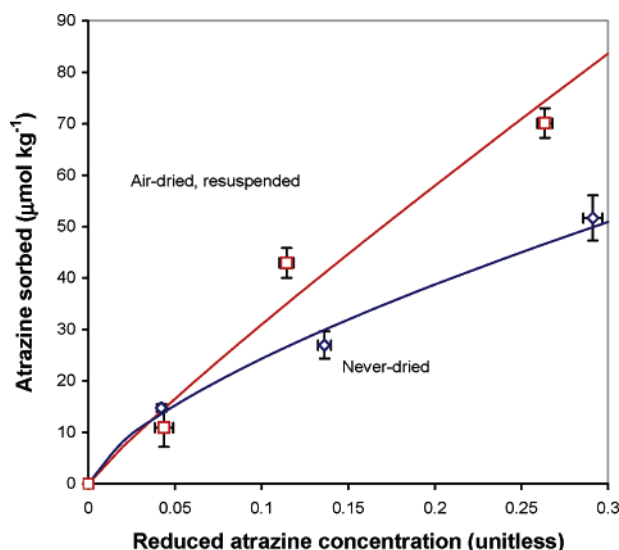


FIGURE 4. An example of the atrazine sorption isotherm obtained for the smectitic soils (Sparta in 10 mM CaCl_2). Reduced concentrations are concentrations normalized by the aqueous solubility (29).

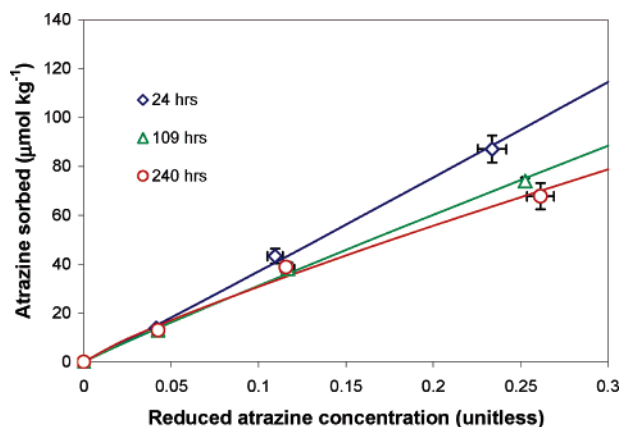


FIGURE 5. The effect of rehydration time for the air-dried Sparta soil (in 10 mM CaCl_2) on atrazine sorption. Reduced concentrations are concentrations normalized by the aqueous solubility (29).

TABLE 3. Regression Coefficients Calculated from the Nonlinear Fit of the Modified Freundlich Equation to the Atrazine Sorption Data for the Air-Dried, Resuspended Sparta Soil in 10 mM CaCl_2

rehydration time (h)	24	109	240
$K_F'(t)$	395	278	221
$K_F'(t)$ st. error	10	6	10
$n(t)$	1.03	0.95	0.86
r^2	1.00	1.00	0.99

K_F' values for the ND Sperry and ND Zook soils. These results indicate that air-drying treatments and choice of background electrolyte can significantly impact atrazine sorption for smectitic soils. The results, however, were not entirely consistent with the trends observed using the Panther Creek smectite.

The effect of soil rehydration time (prior to atrazine addition) on atrazine sorption was studied using the AD Sparta soil suspended in CaCl_2 (Figure 5). These data show that the $K_F'(t)$ values were significantly lower after a 240-h rehydration time relative to a 24-h rehydration time (Table 3). The $n(t)$ values also decreased with rehydration time. Enhanced sorption of atrazine on previously air-dried soil has been shown to occur when a solute moves with a wetting

front (25, 35). Our data show that the legacy of an air-drying treatment may influence atrazine sorption long after a sample has been rehydrated. In practical terms, the data demonstrate that sample handling can have a substantial impact on sorption of atrazine and probably many other organic compounds by soils and clays and therefore should be carefully considered in both mechanistic studies of sorption phenomena and efforts to model the environmental fate of contaminants in soils and sediments.

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Supporting Information Available

Two tables showing statistical comparisons of the K_F' values for the different atrazine sorption isotherms and one figure showing the X-ray diffraction data of the soils used in this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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